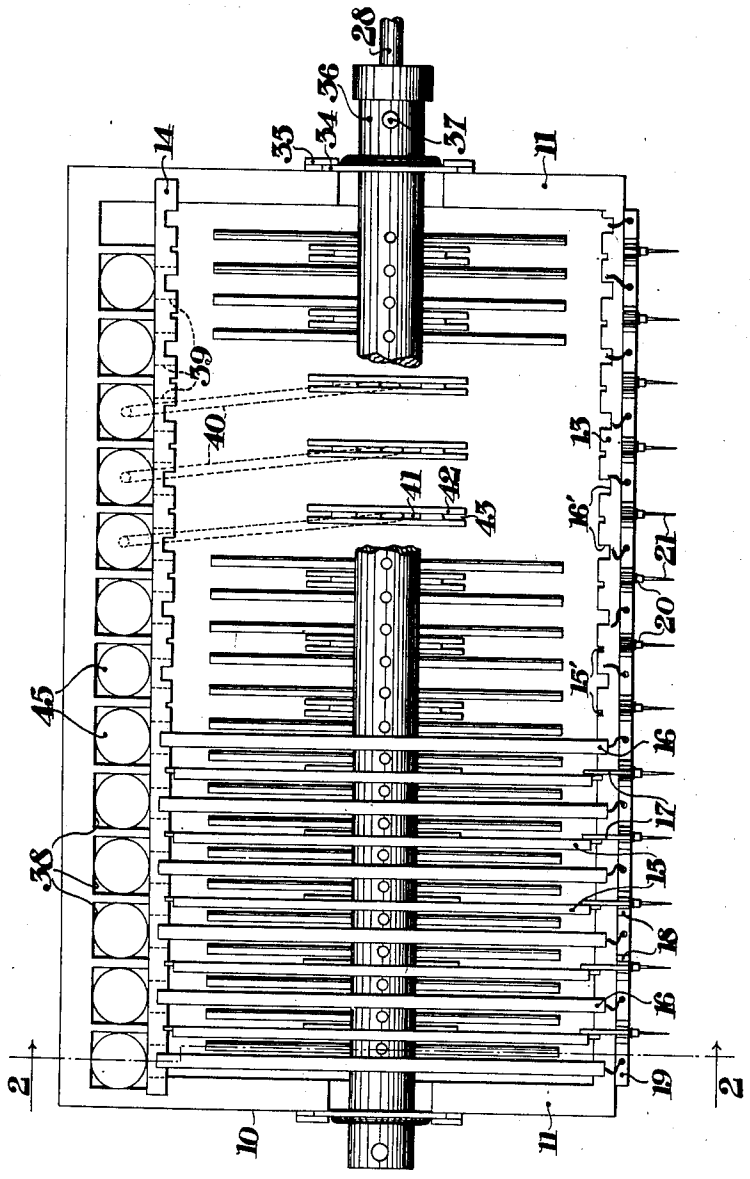
May 22, 1934. K. C. D. HICKMAN ET AL 1,959,531

APPARATUS FOR ELECTROPLATING SILVER FROM USED PHOTOGRAPHIC FIXING SOLUTIONS

Filed May 28, 1931 2 Sheets-Sheet 1

Fig. 1.



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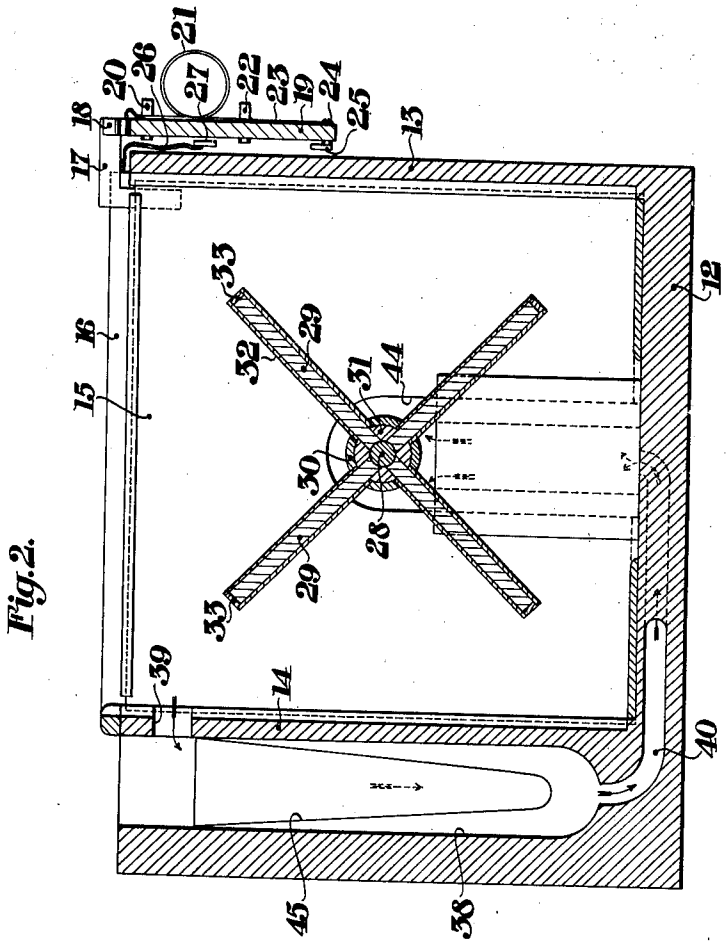


Fig. 2.

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APPARATUS FOR ELECTROPLATING SILVER FROM USED PHOTOGRAPHIC FIXING SOLUTIONS

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Application May 28, 1931, Serial No. 540,621

10 Claims. (Cl. 204—5)

The present invention relates to an electroplating apparatus, and more particularly to a plating cell for used or exhausted photographic fixing solutions.

Up to the present time, the sizeable amounts of silver existing in used fixing solutions as silver thiosulfate, have been recovered from those solutions by chemical processes which precipitate the silver out of the solution in the form of a sludge which may be dried or evaporated with considerable lapse of time. Such a sludge, however, contains only from 40% to 70% of silver and is of relatively low commercial value. Furthermore, the chemical reaction necessary to precipitate the silver from the fixing solutions may render the fixing solution useless for photographic purposes.

It is also understood that recovery of silver from fixing solutions by electrolysis has been attempted at various times. Due, however, to the fact that the reactions during such electrolysis are prone to produce silver sulfide at the cathode to contaminate the deposit, it has not been feasible to use any of the known electrolysis apparatus in commercia practice.

In our co-opending application relating to the method of Recovering silver from used photographic fixing solutions by electrolysis, Serial No. 540,622 filed May 28, 1931, we expose at some length the theory underlying our conclusion that violent mechanical agitation of the electrolyte is necessary for good silver plating from used fixing solutions, as distinguished from a silver plating process for used fixing solutions which provides for agitation of the electrolyte by aeration or passage of air therethrough across the surface of the electrodes.

The primary object of the present invention is the provision of an electroplating apparatus which provides mechanical agitation of the electrolyte across the surface of the electrodes, which mechanical agitation is very necessary for good results.

Another object of the present invention is the provision of a mechanical agitation means for an electrolplating apparatus which comprises a rotor having arms which move adjacent to the electrodes of the apparatus, said rotor and arms being covered with a corrosion resistant material.

A further object of my invention is the provision of a conduit means connected to the casing of the electroplating apparatus for circulation of the electrolyte therethrough.

Still another object of the present invention is the provision of a conduit means which cooperates with the mechanical agitating means of the electroplating apparatus to form a centrifugal pump.

A still further object of the present invention is the provision of a conduit means cooperating with the mechanical agitating means to form a centrifugal pump and to simultaneously provide a convenient location for a filter means to strain the electrolyte.

With these objects in view, the present invention consists in certain features of novelty in the construction, combination and arrangement of parts by which the said objects and certain other objects are effected, all as fully described with reference to the accompanying drawings and more particularly pointed out in the claims.

Like reference numerals designate similar elements in said accompanying drawings wherein:

Figure 1 illustrates a top view of the electroplating apparatus according to the invention, but with the electrodes removed in part and with a fragment removed from the mechanical agitating means to promote the clarity of the illustration.

Figure 2 is a transverse section through the plating apparatus according to the invention taken on the cutting plane 2—2 of Figure 1.

In the illustrated embodiment of the invention, the casing 10 is preferably rectangular in form and comprises ends 11, a bottom 12, a side 13, and a side 14.

A plurality of stainless steel cathodes 15 and carbon anodes 16 are mounted within the casing 10 and are held in spaced relation within casing 10 by means of respective grooves 15' and 16' provided in the sides 13 and 14 of the casing. The carbon anodes 16 divide the casing into $(n+2)$ compartments comprised of n compartments between each of the anodes 16 and two end compartments having one wall thereof formed by the ends 11 of the casing. A plurality of or n cathodes 15 are centrally located in each of the n compartments and are connected by bars 17 to switch clips 18 mounted on the edge of a panel board 19 which is attached to the side 13 of the casing.

The panel board 19 has a set of binding posts 20 which are attached to each of the switch clips 18. Resistance coils 21 are each connected to binding posts 20 and to a second set of binding posts 22 centrally located on the panel board 19. A set of shunt wires 23 are connected between binding posts 22 and a plurality of bolts 24, which are connected to a bus bar 25 mounted on the rear of the panel board 19. Each of the anodes 16 is connected by a flexible wire 26 to a

second bus bar 27, also mounted on the rear of panel board 19.

Except for the electrodes of the apparatus, panel board 19 contains all of the circuits for the apparatus. The cathode bus bar 19 and the anode bus bar 27 are connected, respectively, to the negative and positive sides of a direct current generator (not shown). The direct current passes in parallel through each of the flexible wires 26 to the anodes 16 and then passes through the electrolyte, which is contained in the casing, to each of the cathodes 15 from whence the current passes through the bars 17, switch clips, resistance coils 21, and shunts 23 to the cathode bus bar 25. The shunts 23 facilitate the determination of the plating current through any individual pair of anodes and cathodes by the attachment of a millivoltmeter across each end of shunt 23.

The electroplating apparatus so far described is of well known construction but would not function successfully to plate silver from a used fixing solution unless operated at extremely low and impractical voltages or current densities. The features of the apparatus which make commercial plating possible, and which constitute the greater part of the invention, are described hereinafter:

A mechanical agitating means is moved within the electrolyte of the plating apparatus to violently agitate the electrolyte and to sweep the same across the surfaces of the electrodes. Such a mechanical agitating means may comprise a rotor including a shaft 28 having a plurality of arms 29 mounted thereon, the arms 29 are provided in sets spaced axially on the shaft 28, two sets of arms being located within each of the n compartments within the casing. Each set of arms in itself preferably comprises four arms 29 attached in quadrature to the shaft 28. There is a set of arms 29 between every anode and cathode but none in the end compartments of the casing.

Inasmuch as the mechanical agitating means is adapted to rotate within a used photographic fixing solution which is highly corrosive, the rotor is completely covered with a corrosion resistant material. This is accomplished by placing a hard rubber tube 30 around the shaft 28 and providing sectors 31 of soft rubber to fill the space between the shaft 28 and the tube 30. The arms 29 are each covered with rubber tubes 32 connected or vulcanized to the tube 30 at one end and to plugs 33 at the other end.

The corrosive action of the used fixing solution employed as an electrolyte complicates the arrangement of bearings for the mechanical agitating means. This problem is specifically dealt with in the co-pending application of K. C. D. Hickman for Improvements in bearing construction and mounting therefor, Serial No. 540,619, filed May 28, 1931.

The bearing construction, however, is indicated broadly in Figure 1 and includes a rubberized flexible canvas wall 34 attached to the outside ends 11 of the casing by means of U-shaped strips 35 and a stuffing gland assembly 36 attached to wall 34 and provided with a grease cup 37. The mechanical agitating means may be rotated in any suitable manner such as by a belt drive to a pulley (not shown) on shaft 28.

The mere agitation of the electrolyte within the casing and across the surfaces of the electrode is, in itself, not sufficient to insure the best deposit on the cathodes 15. Consequently, a conduit means for cooperation with the mechanical agitating means to form a centrifugal pump for the electrolyte is provided. The conduit means includes a plurality of n cells 38 which are located along the side 14 of the casing. The cells 38 each have an inlet 39 provided in the wall 14 of the casing and at approximately the level of the electrolyte in the casing. The rotation of the agitating means, in a counter-clockwise direction viewed from Figure 2, causes circulation of the electrolyte within the compartments and through the inlets 39 to the individual cells 38. The electrolyte is returned from the cells 38 by a plurality of ducts 40 in the bottom 12 of the casing. The ducts 40 lead to a rectangular channel 41 within a standpipe 42 which has an outlet subjacent to the shaft of the agitating means. The standpipes 42 have grooves 43 in the edges thereof and are each located in the center of the individual compartments so that the grooved edges thereof support the cathodes 15.

The cathodes 15 and the anodes 16 are all provided with inverted U-shaped slots 44 so that they may straddle the rotor of the mechanical agitating means. The cathodes 15 being of stainless steel are thin and tend to swing out of position within the casing. Therefore, they are held in position by slots in the bottom 12 of the casing and, also, by the previously described grooved edges of the standpipes 42. The bottom edges of the anodes 16 are also placed in grooves in the bottom 12 of the casing.

The conduit means provides a very convenient place for filtering the electrolyte as it passes therethrough. This filtering may be accomplished in any of the well known manners but is preferably accomplished by the use of a plurality of felt socks 45 placed in each of the cells 38. Such filtering of the electrolyte is quite necessary because of secondary reactions which take place in the electrolysis of the complex used fixing solution, and is of primary importance in removing any silver sulfide from the electrolyte which may be possibly formed at the cathodes of the apparatus.

The operation of the electroplating apparatus according to the invention will now be described. The anode bus bar 27 and the cathode bus bar 19 are properly connected to a source of direct current energy. The current density necessary from this source of energy depends upon the plating ion concentration of the electrolyte as well as upon the rate at which the electrolyte is circulated within each compartment. Since the plating or silver ion concentration of the solution is lowered during passage of the electrolyte through the cell, the permissible current density is also decreased and it is consequently necessary to reduce the current density progressively along the electrodes in the direction of electrolyte flow by replacing resistance coils 21 with other coils 21 of greater resistance. The mechanical agitating means is rotated from an external variable speed prime mover so that the rate of flow of electrolyte across the surfaces of the electrodes may be varied between one and four feet per second.

Since there are no rotating arms in the end compartments of the casing, the level of electrolyte therein is lower than in the remaining compartments. Therefore, the electrolyte is introduced into the apparatus at these end compartments and is preferably drawn off from the cell by a siphon or other drainage means (not shown) at the center of the casing.

This manner of introducing and removing the

electrolyte from the apparatus is made possible by the series connection of the compartments through the open portions of the inverted U-slots 44 in all of the electrodes.

The path of the electrolyte within each compartment is better understood from Figure 2. The mechanical agitating means causes some of the electrolyte to flow through conduit means inlet 39, through the filter means such as felt sock 45, through the duct 40 and rectangular conduit 41 of the standpipe 42 having an outlet just below the shaft of the agitating means. The rotation of arm 29 swirls the water between the electrode so that there is a low pressure area adjacent the shaft of the agitating means and adjacent the outlet of the standpipe 42. Therefore electrolyte will be drawn through the standpipe and circulated through the inlet 39 and conduit means in an endless path.

The successful operation of the apparatus according to the invention depends upon the care of the cathodes 15 and the filter bags 45. Stainless steel is used for cathodes 15 to receive the silver because of its stability toward used fixing solutions, its strength, and the difficulty with which adherent silver deposits are obtained. This property secures ease of stripping. The electrodes should be cleaned with soap powder, rinsed thoroughly, dried and polished with a rag moistened with gasoline containing a trace of heavy oil. They are then placed in the cell which should be full of used fixing solution containing at least one part of silver per thousand of solution. Electrolysis may be commenced at 100 amperes and the current raised if the deposit appears bright after an hour. When, at any time, an over-supply of current dulls the electrodes the current should be reduced to 50 to 100 amperes, till the surface has brightened again. If the surface persists in remaining rough and dull, the electrodes should be withdrawn and cleaned with soap powder and returned for replating. Occasionally, a serious overdose of current is given to a bath almost depleted of silver, causing blackening of the electrodes and the simultaneous production of brown hypo. The current should be lowered to 10 to 20 amperes, the supply of used fixing solution shut off, and the agitating means allowed to rotate until practically all the color has been removed by the filters. If the cathodes now appear smooth, the flow of solution and current may be increased until plating is proceeding normally. The longer the cathode surfaces can be maintained bright the thicker the deposit that can be built up without the labor of cleaning.

The filter bags 45 may become clogged occasionally from impurities in the electrolyte when it reaches the cells, and from silver sulfide sometimes generated during plating. When it is apparent that little filtering is taking place, the bags should be withdrawn, turned inside out, and rubbed vigorously under the surface of water. They should now be whitish in appearance and free from loose deposit, and they may be returned to the cells in the inside-out condition. Next washing they will again be reversed.

The brown sludge washed from the filter bags 45 is allowed to settle and is occasionally drawn off, dried in shallow pans and sold to the refiners. Alternatively, it may be dissolved in nitric acid, reprecipitated with sodium carbonate, redissolved in fixing solution, and electrolyzed. The quantity of this relative sludge to the total silver handled is very small.

In the present apparatus, the current density is usually high, and the deposit is a composite material which contracts on drying. To remove the silver the electrodes are washed, dried with or without gentle heat, and stripped. Gentle bending or tapping detaches part of the silver and the remainder is pried off with a blunt tool.

Since many modifications of the electroplating apparatus according to the invention are possible, especially in providing a mechanical agitating means and conduit means, this disclosure is to be construed as covering all equivalent elements for accomplishing the same functions, the scope of the invention being pointed out particularly in the appended claims.

Having now particularly described our invention, what we claim and desire to secure by Letters Patent of the United States is:

1. In an electro-plating apparatus, the combination with a casing containing a plurality of spaced electrodes and adapted to contain a used photographic fixing solution as electrolyte, of a mechanical agitating means including a shaft extending centrally through the casing and electrodes, arms on said shaft adapted to rotate adjacent and between said electrodes and adapted to swirl the electrolyte across the surfaces of the electrodes, and a coating of rubber on said shaft and arms.

2. In an electro-plating apparatus, the combination with a casing containing a plurality of stationary carbon anodes and stationary stainless steel cathodes in spaced relation, said casing being adapted to contain used photographic fixing solution as an electrolyte, of a mechanical agitating means located adjacent said anodes and cathodes, and adapted to sweep the electrolyte across the surfaces of the stationary anodes and stationary cathodes.

3. In an electro-plating apparatus, the combination with a casing containing a plurality of spaced electrodes forming compartments and adapted to contain an electrolyte, of a mechanical agitating means including a plurality of arms adapted to move adjacent and between said electrodes and adapted to sweep the electrolyte across the surfaces of the electrodes, the end compartment in the casing having no arms of the agitating means and being adapted to contain electrolyte at a lower level than in the remaining compartments.

4. In an electro-plating apparatus the combination with a casing containing a plurality of spaced electrodes and adapted to contain an electrolyte, of a mechanical agitating means located adjacent said electrodes and a conduit means cooperating with said agitating means so that the same is adapted to sweep electrolyte over the surfaces of said electrodes and to circulate electrolyte through said conduit means.

5. In an electro-plating apparatus, the combination with a casing containing a plurality of spaced electrodes and adapted to contain an electrolyte, of a mechanical agitating means located adjacent said electrodes and a conduit means cooperating with said agitating means to form a centrifugal pump for the electrolyte while causing the same to sweep over the surfaces of the electrodes.

6. In an electro-plating apparatus, the combination with a casing containing pairs of spaced anodes, each pair forming a compartment containing a cathode, said casing and compartment being adapted to contain an electrolyte, of a mechanical agitating means located adjacent said anodes and cathodes, and conduit means each

connected at one end to the top of each compartment and at the other end to the center of each compartment.

7. In an electro-plating apparatus, the combination with a casing containing pairs of spaced anodes, each pair forming a compartment containing a cathode, said casing and compartment being adapted to contain an electrolyte, of a mechanical agitating means located adjacent said anodes and cathodes, and conduit means each including cell connected to the top of each compartment and including a standpipe connected to the bottom of each cell and having an outlet adjacent said agitating means.

8. In an electro-plating apparatus, the combination with a casing containing pairs of spaced anodes, each pair forming a compartment containing a cathode, said casing and compartment being adapted to contain an electrolyte, of a mechanical agitating means located adjacent said anodes and cathodes, and conduit means each including a cell containing a filter means and connected to the top of each compartment and including an outlet adjacent said agitating means.

9. In an electro-plating apparatus, the combination with a casing containing pairs of spaced anodes, each pair forming a compartment containing a cathode, said casing and compartment being adapted to contain an electrolyte, of a mechanical agitating means including a rotor having a plurality of arms adapted to rotate adjacent and between said anodes and cathodes which are provided with slots to straddle said rotor, and conduit means each having an inlet from the top of each compartment and each including a standpipe forming the outlet for the conduit means and abutting the edges of the slot in the cathodes to support the same.

10. In an electro-plating apparatus, the combination with a casing containing pairs of spaced anodes, each pair forming a compartment containing a cathode, said casing and compartment being adapted to contain an electrolyte, of a shaft extending centrally through the casing, anodes and cathodes, a set of arms in quadrature on said shaft and between each pair of anodes and cathodes, two sets in each compartment, an external cell for each compartment and provided with an inlet at the top of each compartment and a standpipe with grooved edges engaging the cathodes in each compartment, connected to the bottom of said cell and having an outlet subjacent to said shaft.

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